CALCULATIONS SUGGEST NEW ROUTES TOWARDS HIGH CAPACITY HYDROGEN STORAGE MATERIALS

Developing safe, cost-effective, and practical means of storing hydrogen is crucial for the advancement of hydrogen and fuel-cell technologies. The discovery of enhanced reversible hydrogen sorption by Ti-doped alanates [1] opened up an entirely new prospect for lightweight hydrogen storage. However, in spite of the extensive investigations of alanates, little is known about the mechanism by which Ti enhances the cycling kinetics of hydrogen. In fact, even the location of the Ti atoms remains unclear. To shed some lights on these issues, we have studied structure and dynamics of pure and Ti-doped alanates using first-principles quantum calculations and inelastic neutron scattering techniques [2].

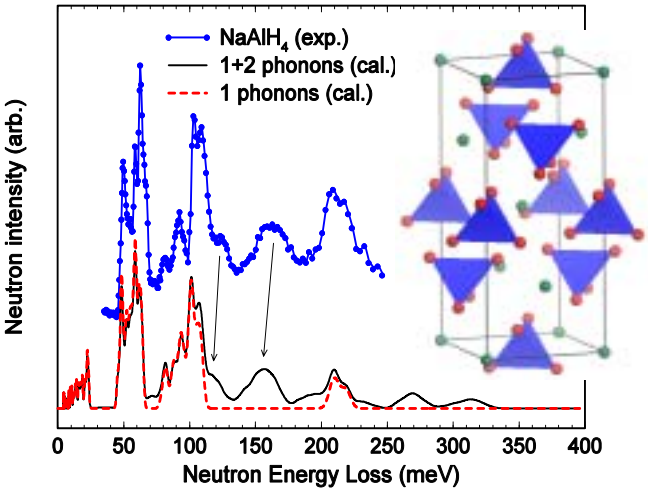

Figure. 1 Measured (top) and calculated (bottom) INS spectra of $NaAlH_4$. The calculated 1 and 1+2 phonon contributions are shown. The structure of $NaAlH_4$ is shown in the inset; blue tetrahedral represent AlH_4 units.

Figure 1 shows the vibrational spectra of sodium alanate, $NaAlH_4$, which exhibits several sharp phonon bands up to 250 meV. In the same figure we also show the calculated one-phonon spectrum, which clearly fails to explain many features in the data. However, including two-phonon scattering processes yields a result that is in excellent agreement with the data. Such strong and sharp multi-phonon contributions are unusual, and could have been easily mistaken as single phonons if we had not had the theoretical results. The calculations also indicate the nature of the different phonon bands in Fig.1. The low energy modes are AlH_4 translations, while those around 50 meV are rotations. The modes above 200 meV consist of stretching modes of AlH_4 tetradedron. The modes between 75 meV and 125 meV are mixtures of rotations and stretches.

The excellent agreement between the neutron data and our calculations suggest that the first-principles methods describe the alanate systems accurately and therefore can be used to make predictions. We therefore extend our calculations to investigate the possibility of substitutional Ti doping of alanates, as well as the effect of the dopant on the surrounding hydrogen dynamics and bonding.

From the many substitutional and interstitial doping models that could be tried, we choose two that are experimentally motivated, i.e. the substitution of Al and Na by Ti. In the following we denote these doping models by ``**Ti→Al**" and ``**Ti→Na**", respectively. We consider supercells containing 16 $NaAlH_4$ formula units, and substitute only one of the Al or Na atoms by Ti. The cohesive energies are obtained as the sum of the individual atom energies minus the energy of the system (see Table 1). We find both **Ti→Na** and **Ti→Al** are energetically more stable than pure alanate; i.e. the system gains energy by accepting a Ti dopant into the bulk and releasing a Na or Al atom. In addition, **Ti→Na** is found to be the most favorable substitution.

It may seem surprising that **Ti→Na** has a higher cohesive energy than **Ti→Al**. The typical valences of these atoms certainly suggest otherwise. However, Ti seems to be relatively large for the Al site. This size mismatch is the most likely cause for **Ti→Al** to be energetically less favorable.

The relaxed **Ti→Na** structure presents H atoms that come close to the Ti dopant. The shortest Ti--H distance is 2.05 Å, compared with the 2.39 Å Na--H distance in the pure system. This result suggests that Ti dopants may facilitate the breaking of the Al--H bond. We explored this possibility by moving one H atom to the immediate vicinity of the dopant and then relaxing the system. The resulting structure (see Fig. 2), which we denote by ``**Ti→Na (H)** ", is considerably more stable than the original **Ti→Na** doping model. In fact, we found that it

has not one but two H atoms very close to the Ti. The shortest Ti--H distance is 1.81 Å , and the corresponding Al--H distance is 1.89 Å, i.e. 0.25 Å longer than in pure $NaAlH_4$. Thus the Ti dopant can indeed induce Al--H bond breaking, a necessary step for H_2 release.

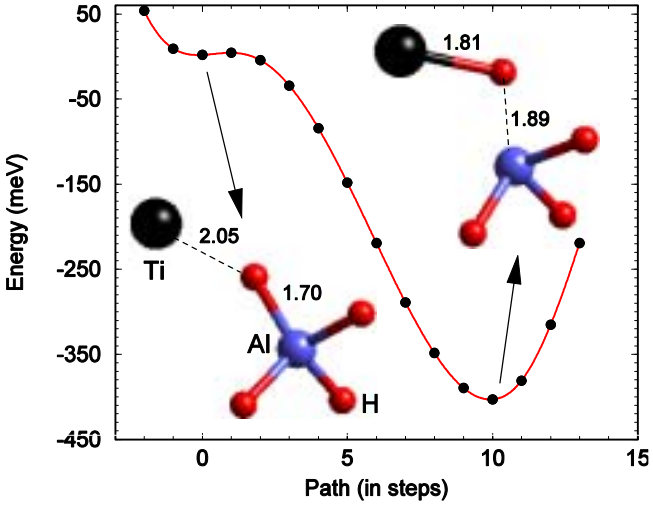

Figure 2. Energy along the path from Ti → Na to Ti → Na (H) structures. Insets shows the local structure and bond distances at the two minima.

Along these lines, we also considered a less obvious possibility, namely, that Ti drags extra hydrogens into the system. We model this case by placing one extra H in the vicinity of the Ti atom. This structure, which we denote by "**Ti→Na+H** " in Table 1, turns out to be the most stable of the doped systems considered. We find a Ti--H bonding distance of 1.82 A and several AlH_4 groups approaching the Ti dopant.

Systems	Ti→Al	Ti→Na	Ti→Na(H)	Ti→Na+H
E_{coh}(eV)	0.075	0.911	1.316	1.317

Table 1. Calculated atomic cohesive energies per 96-atom unit cell for different doped systems. The result for pure $AlNaH_4$ (231.922 eV) is taken as the zero of energy.

Finally, we study the effect of the Ti dopants on the vibrational spectrum of neighboring AlH_4 groups. We find that Ti dopant mainly affects the high-frequency modes near 200 meV, i.e. those involving stretching of the AlH_4 tetrahedron. All the modes in that group soften differently for the **Ti→Na** and **Ti→ Al** cases. This suggests that, by investigating the phonon spectrum of Ti-doped $NaAlH_4$, one might determine whether Ti dopants go into the bulk of the system and, if so, where they are located. Motivated by this possibility, we measured the phonon spectrum of a 2% Ti-doped sample, but obtained a result essentially identical to that of pure alanate shown in Fig.1. However, it should be noted that this does not rule out the possibility of substitutional doping in our sample since the amount of Ti is very small, and thus any dopant-induced feature in the spectrum should also be very small and hard to distinguish from the noise. In addition, the NIS spectrum of pure sodium alanate presents significant two-phonon intensity in the 175-200 meV energy range (see Fig. 1), which makes it difficult to identify fine details. Higher resolution spectroscopic measurements, such as Raman scattering, might help elucidate this issue.

In conclusion, we have used *ab initio* quantum mechanics calculations and inelastic neutron scattering (INS) measurements to study pure and Ti-doped sodium alanate ($NaAlH_4$), a material that holds great promise for reversible hydrogen storage. The calculations indicate that the Ti dopant prefers to substitute for Na and attracts several hydrogen atoms, softening and breaking the corresponding Al-H bonds. Even more interestingly, we found it energetically favorable for the Ti to drag extra H atoms into the system. These results point to an interesting direction for future research, namely the possibility of producing a new material, sodium-titanium alanate that might benefit from the ability of Ti to accommodate extra hydrogens in its vicinity and thus exhibit improved H-storage capabilities.

REFERENCES

[1] B. Bogdanovic and M. Schwickardi, J. Alloys Comp. **253**, 1 (1997).

[2] Jorge Íñiguez, T. Yildirim, T. J. Udovic, M. Sulic, and C. M. Jensen, Phys. Rev. B **70**, R060101 (2004).